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XIII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
HARVARD COLLEGE.A NEW METHOD FOR THE QUANTITATIVE
DETERMINATION OF HYDROXYL.

BY C. LORING JACKSON AND G. W. ROLFE.

THE methods now in use for determining the number of hydroxyl radicals in a molecule can be divided into two classes,—those which consist in the analysis of the acetyl or benzoyl compound, and those which depend on the saponification of the acetyl compound and the quantitative determination of one or other of the products of the decomposition. Methods of the first class cannot be applied to substances having large molecular weights, as then the differences in percentage composition approach the limit of error of the analysis; and even methods of the second sort have led to false conclusions in many cases, (for instance, with æsculine and æsculetine, which give soluble compounds with magnesian hydrate,) or are inapplicable, owing to the instability of the compound with saponifying agents. We have worked out, therefore, a new method for determining hydroxyl quantitatively, which is applicable in cases where the methods now in use can be applied only with difficulty or give uncertain results, and, we hope, will commend itself also in other cases on account of its simplicity, as it does away with the additional operation of saponification—often a tedious one—necessary in methods of the second class.

Our process consists in converting the substance into its parabrombenzoyl compound, and determining the amount of bromine introduced by an analysis according to the method of Carius. It therefore belongs with methods of the first class, but has the advantage that the differences in percentage composition are larger than when carbon and hydrogen are determined in the benzoyl or acetyl compounds, as is shown by the following comparison of the differences caused by the presence of one more hydroxyl in the molecule between the percentages of carbon in the benzoyl and of bromine in the brombenzoyl

derivatives of æsculetine, æsculine, and fisetine,* substances which we have selected for calculation on account of the differences in their molecular weights.

Name and Formulas of Substance.	Benzoyl Compound. Difference in % of C.	Brombenzoyl Compound. Difference in % of Br.
Æsculetine, $\left. \begin{array}{l} \text{C}_9\text{H}_3\text{O}(\text{OH})_3 \\ \text{C}_9\text{H}_4\text{O}_2(\text{OH})_2 \end{array} \right\}$	1.97	3.60
Æsculine, $\left. \begin{array}{l} \text{C}_{15}\text{H}_{10}\text{O}_3(\text{OH})_6 \\ \text{C}_{15}\text{H}_{11}\text{O}_4(\text{OH})_5 \end{array} \right\}$	0.90	1.50
Fisetine, $\left. \begin{array}{l} \text{C}_{23}\text{H}_{10}\text{O}_3(\text{OH})_6 \\ \text{C}_{23}\text{H}_{11}\text{O}_4(\text{OH})_5 \end{array} \right\}$	0.78	1.66

The numbers given in the third column of the above table are far enough removed from the maximum analytical error to leave no doubt in regard to the composition of the substance; and we may add, that, as far as our experiments go, the parabrombenzoates show a much greater tendency to crystallization than the corresponding benzoates, so that in most cases the error from incomplete purification can be reduced to a minimum.

In deciding which acid containing bromine was the best adapted to our purpose, we rejected the fat acids, although, other things being equal, they were to be preferred on account of the greater differences in the percentages of bromine, because we feared the removal of a portion of the bromine in the preparation or purification of the ester, and accordingly selected from the aromatic acids that one which we found could be prepared most easily, that is, the parabrombenzoic acid.

In the remainder of the paper we give the details of the methods which we found most convenient for the preparation of the parabrombenzoic acid, and its chloride and anhydride, as well as a few experiments on the formation of parabrombenzoyl esters, undertaken to determine whether these bodies could be formed as easily as the corresponding benzoyl compounds, but we have not considered it necessary to extend these experiments to the less accessible substances, or to multiply them for the commoner bodies, as those which we have tried are sufficient to prove the general application of the method; showing that the parabrombenzoylchloride is as reactive as benzoylchloride, and

* Schmid, Ber. d. ch. G., 1886, p. 1351.

that the anhydride, although on account of its high melting-point somewhat less manageable than the non-substituted one, acts excellently on all substances which can stand a high temperature, and can usually be made to act on those which cannot by heating with anhydrous benzol in a sealed tube. As all the derivatives of parabrombenzoic acid described in this paper, with the exception of the chloride, are new, we give a full account of their properties, as a contribution to our knowledge of this hitherto neglected acid.

Preparation of Parabrombenzoic Acid.

Although this method offers no new features, we think it best to describe it as a matter of convenience for those who may wish to obtain the acid in quantity. The first step is the preparation of crude monobromtoluol by mixing toluol with ten per cent of its weight of iodine and the calculated amount of bromine. After the mixture has stood at the ordinary temperature for twelve hours, the product is washed with sodic hydrate and water, the bromtoluol fractioned, and the portion boiling from 180° to 190° oxidized by boiling 150 gr. of it in a flask with a return-condenser for twelve hours with 400 gr. of potassic dichromate and 550 gr. of sulphuric acid diluted with twice its bulk of water. The unoxidized oil, consisting of orthobromtoluol with a little para, is distilled off with steam, and the acid purified by washing with water and conversion into the sodic salt. The product is free from the isomeric brombenzoic acids, as shown by its melting point, $248-250^{\circ}$ (uncorr.). The yield varied from 40 to 70 per cent of the weight of crude bromtoluol used, and a preparation can be carried through from toluol to the pure acid in less than one week.

Parabrombenzoylchloride, $C_6H_4BrCOCl$. — This substance has been prepared by J. W. Raveill,* under the direction of Hübner; but he gives only the most meagre description of it, stating that it forms colorless, easily fusible, volatile needles. It is prepared without difficulty by heating a mixture of phosphoric pentachloride and the dry acid in a flask to 100° until the reaction has ceased, when the temperature is to be raised to 150° , and kept at this point until the greater part of the phosphoric oxychloride formed has passed off. The chloride is then extracted with ligroine and purified by distillation. The yield is about 80 per cent. Its composition was determined by the following analyses:—

* Ann. Chem., ccxxii. 178, note.

- I. 0.4010 gr. of the substance gave on combustion 0.5575 gr. of carbonic dioxide and 0.0745 gr. of water.
- II. 0.2273 gr. gave by the method of Carius 0.3448 gr. of the mixture of argentic chloride and bromide.
- III. 0.4160 gr. gave by the same method 0.6278 gr. of the mixture of argentic chloride and bromide.
- IV. 0.3014 gr. gave, when boiled with a solution of pure potassic hydrate, after acidification with nitric acid and precipitation with argentic nitrate, 0.1962 gr. of argentic chloride.
- V. 0.4284 gr. gave by the same method 0.2773 gr. of argentic chloride.

	Calculated for $C_6H_4BrCOCl$.	I.	II.	Found. III.	IV.	V.
Carbon	38.26	37.92				
Hydrogen	1.82	2.06				
Chlorine and bromine	52.62	. . .	52.61	52.86		
Chlorine	16.17	16.08	16.01

Properties. — White needles with an odor similar to that of benzoylchloride, but much less marked, owing to its higher boiling point; melting point, 30° . It boils at $245\text{--}247^\circ$ * (uncorr.) with slight decomposition; water does not dissolve it, and acts upon it very slowly, if at all, in the cold, more rapidly when boiling; it is easily soluble in ligroine or benzol, while alcohol dissolves it with conversion into the ethylester, a viscous liquid with an odor similar to that of oil of anise.

Parabrombenzoic Anhydride, $(C_6H_4BrCO)_2O$. — This substance was prepared by heating the sodic parabrombenzoate with parabrombenzoylchloride not in excess; convenient proportions are 3 gr. of the sodic salt to 2 gr. of the chloride. The mixture was heated in a flask with an air-condenser for an hour to 200° by means of a paraffine bath, and the product purified by washing, first with ligroine, then with a strong solution of sodic carbonate, and finally with benzol to remove the tarry impurities. The yield was about 50 per cent. Owing to its very slight solubility in all the common solvents, we did not attempt to purify it by crystallization, but this was fortunately unnecessary as the following analyses show that the substance purified as above by washing is essentially pure.

* It was not thought worth while to try to determine this temperature with greater accuracy, because of the decomposition with which the boiling is accompanied.

- I. 0.2310 gr. of the substance gave by the method of Carius 0.2260 gr. of argentic bromide.
 II. 0.2167 gr. gave 0.2138 gr. of argentic bromide.

	Calculated for (C ₆ H ₄ BrCO) ₂ O.	Found.	
		I.	II.
Bromine	41.67	41.64	41.99

Properties. — As obtained by the method described above, it forms an odorless, bulky, white powder; crystallized from chloroform, it forms minute oblong rectangular plates; from benzol, small pointed needles; melting point, 212–213°. It is insoluble in water, and apparently not decomposed by it even when boiling; almost insoluble in ether, glacial acetic acid, or carbonic disulphide; slightly soluble in benzol, somewhat more so in chloroform, which is the best solvent for it; hot alcohol dissolves it freely, converting it into the ethylester, as shown by the characteristic odor of that substance. Cold sodic hydrate is essentially without action on it, but decomposes and dissolves it slowly when warmed with it.

Phenylparabrombenzoate, C₆H₄BrCOOC₆H₅. — This substance was made by heating phenol and parabrombenzoylchloride in a flask with a return-condenser to about 200°. It was also prepared from phenol and parabrombenzoic anhydride at the same temperature. The product, a waxy solid, was purified by crystallization from alcohol, dried at 100°, and analyzed.

- I. 0.1927 gr. of the substance gave by the method of Carius 0.1295 gr. of argentic bromide.
 II. 0.1051 gr. gave 0.0710 gr. of argentic bromide.

	Calculated for C ₆ H ₄ BrCO ₂ C ₆ H ₅ .	Found.	
		I.	II.
Bromine	28.88	28.61	28.76

Properties. — White scales with a pearly lustre somewhat resembling naphthaline; it has a slight agreeable odor, and melts at 117°. It is insoluble in water, readily soluble in alcohol, methyl alcohol, ether, benzol, chloroform, or carbonic disulphide, less so in ligroine, and not freely soluble in glacial acetic acid. Alcohol is the best solvent for it.

Phenylbenzoate is a well-crystallized substance melting at 68–69°.

Pyrogallol Triparabrombenzoate, (C₆H₄BrCOO)₃C₆H₃. — This substance was made by the action of parabrombenzoylchloride on pyrogallol at 100° for six hours. After removing the excess of the chloride with ligroine, the residue was washed with a boiling solution of sodic carbonate, and the slightly yellowish waxy solid purified by crys-

tallization from hot benzol. Its composition was determined by the following analyses:—

- I. 0.1569 gr. of the substance gave by the method of Carius 0.1322 gr. of argentic bromide.
 II. 0.1153 gr. gave 0.0963 gr. of argentic bromide.

	Calculated for $(C_7H_4BrO_2)_3C_6H_5$.	Found.	
		I.	II.
Bromine	35.56	35.85	35.55

Properties.—It forms a white crystalline powder made up of microscopic diamond-shaped plates, which belong to the monoclinic system, to judge from their behavior toward polarized light; melting-point, 140° . Freely soluble in benzol, ether, or chloroform, very slightly soluble in alcohol, glacial acetic acid, or carbonic disulphide, and essentially insoluble in water or ligroine. Hot benzol is the best solvent for it.

It is an important point in favor of our method, that this is a crystalline substance, whereas the product of the action of benzoylchloride on pyrogallol was, according to Nachbaur,* resinous, and the difficulties in the way of its purification were so great that its formula could not be determined with certainty.

Parabrombenzamide, $C_6H_4BrCONH_2$.—This substance was prepared, as a contribution to our knowledge of the derivatives of parabrombenzoic acid, by the action of strong ammoniac hydrate on the parabrombenzoylchloride. The white curdy precipitate thus obtained was purified by three recrystallizations from boiling water. Its composition was determined by the following analyses:—

- I. 0.3012 gr. of the substance gave 18.6 c.c. of nitrogen gas under a pressure of 767 mm. and a temperature of 18° .
 II. 0.1326 gr. of substance gave by the method of Carius 0.1260 gr. of argentic bromide.

	Calculated for $C_6H_4BrCONH_2$.	Found.	
		I.	II.
Nitrogen	7.00	7.20	
Bromine	40.00	. . .	40.44

Properties.—It forms small white rectangular plates with a pearly lustre; melting point, 186° . It is insoluble, or nearly so, in cold water, soluble in hot, and in alcohol, ether, or glacial acetic acid, very slightly soluble in chloroform, and essentially insoluble in ligroine, benzol, or carbonic disulphide.

* Wien. Acad. Ber., xxiv. 270.